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Effect of Photochemical and Photophysical Processes with the Participation of Oxygen on the Luminescent Properties of a Film of a Terbium(III) β-Diketonate Complex

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Abstract—An 18-fold increase in the mean luminescence intensity of Tb^{3+} ions in a vitrified film of a terbium(III) β-diketonate complex under UV laser radiation in atmospheric oxygen at 300 K was observed. Luminescence and Raman spectroscopy data reveal that the observed effect was caused by photophysical and photochemical processes changing the geometry and structure of the complex.

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INTRODUCTION

The combination of unique photophysical characteristics (effective light-transforming capability, monochromatic luminescence with high efficiency and long lifetime) and attractive chemical properties (e.g., relatively easy synthesis, good solubility in organic solvents, and possibility of incorporation into different solid matrices) [1] of lanthanide(III) β-diketonate complexes makes them suitable for fabricating different materials and devices for molecular photonics: optical amplifiers [1], emission layers of organic light-emitting diodes [1, 2], light-transforming coatings [1], luminescent temperature sensors [1, 3], optical oxygen sensors [1, 4], and so on. In the context of practical applications, one of the greatest disadvantages of these compounds is their low resistance to UV irradiation, which irreversibly reduces the intensity of luminescence [5].

We recently reported on a twofold increase in the mean luminescence intensity of Tb^{3+} ions (without subsequent photodegradation) in a vitrified film of a terbium(III) β-diketonate complex under UV laser irradiation at 300 K [6, 7]. In this sample the film was shielded from atmospheric oxygen by two quartz plates. It is well known that oxygen is a quencher of long-lived organic luminophores [8]. Examples of the oxygen quenching of excited states in certain lanthanide(III) β-diketonate complexes are also known [4]. In addition to luminescence quenching, oxygen enhances the rate of photodestruction of complexes upon UV irradiation [9].

In this work, the effect of oxygen on the photophysical and photochemical properties of a vitrified film (supported on a quartz plate) fabricated from a new β-diketonate complex, $Tb(CPDK_{5\text{-}7})_3Phen$ ($CPDK_{5\text{-}7}$ is 1-(4-(4-pentylcyclohexyl)phenyl)decane-1,3-dionato], and Phen is 1,10-phenanthroline; see Fig. 1), was investigated by luminescence and Raman spectroscopy. We have observed that the mean luminescence intensity of Tb^{3+} ions in the film had increased by one order of magnitude (without subsequent photodegradation) after 50 min of irradiation by a pulsed nitrogen laser (337 nm) in the presence of oxygen at 300 K. Such enhancement of luminescence in films of lanthanide(III) β-diketonate complexes had never been reported. The observed effect is therefore of fundamental and practical importance. A detailed study of the nature of this effect, as well as the identification of the factors contributing to its occurrence, could serve as a basis for the development of novel luminescent materials and devices (e.g., optical oxygen sensors) that would not be susceptible to damaging effects of UV radiation.

EXPERIMENTAL

$Tb(CPDK_{5\text{-}7})_3Phen$ powder was synthesized according to the procedure described in [10]. An alcohol solution of 0.039 g $TbCl_3 \cdot 6H_2O$ (0.1 mmol) was added dropwise to a hot alcohol solution containing 0.12 g (0.3 mmol) $CPDK_{5\text{-}7}$, 0.018 g (0.1 mmol) Phen, and 0.017 g (0.3 mmol) KOH while stirring. The light